Radiolysis of Water on Ceramic-Oxide Surfaces

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Introduction

The radiolysis of water adsorbed on oxide surfaces is a major environmental management problem for the storage of mixed waste materials. An oxide of particular importance is PuO_2, which is a long-lived α particle emitter. The self-radiolysis of sealed containers of the wet oxide can lead to hazardous concentrations of H_2 under certain conditions. Radiation chemistry and microdosimetry techniques can give results of direct use for the engineering and management of long-time storage containers.

These experiments also give fundamental knowledge on the radiation chemistry of water in an environment near different ceramic oxides. Energy transfer and other heterogeneous processes in close proximity to surfaces have rarely been examined using basic radiation chemical techniques.

Summary

H_2 yields have been measured from water adsorbed on CeO_2, ZrO_2 and UO_2 irradiated with γ-rays and with 5 MeV He ions.

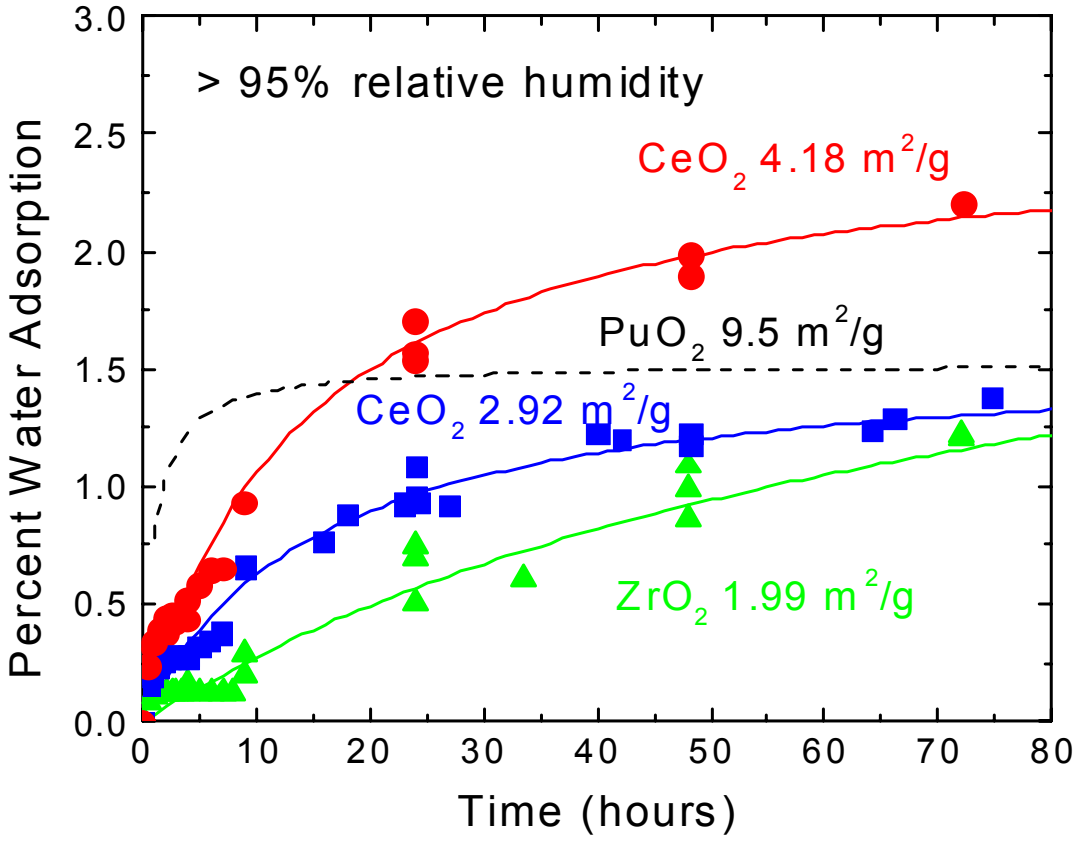
The yields of H_2 with γ-rays appear to depend on the energy escaping the particle surface and the amount of water available.

Mechanism for excess hydrogen yields is unknown - possibly due to migration of electrons / holes or excitons from the oxide to the water layer.

PuO_2 samples have been size characterized and fractional energy loss calculated.

Chemical systems and gaseous microdosimetry techniques are being developed to measure energy escape from PuO_2.

Adsorption of Water on Oxides



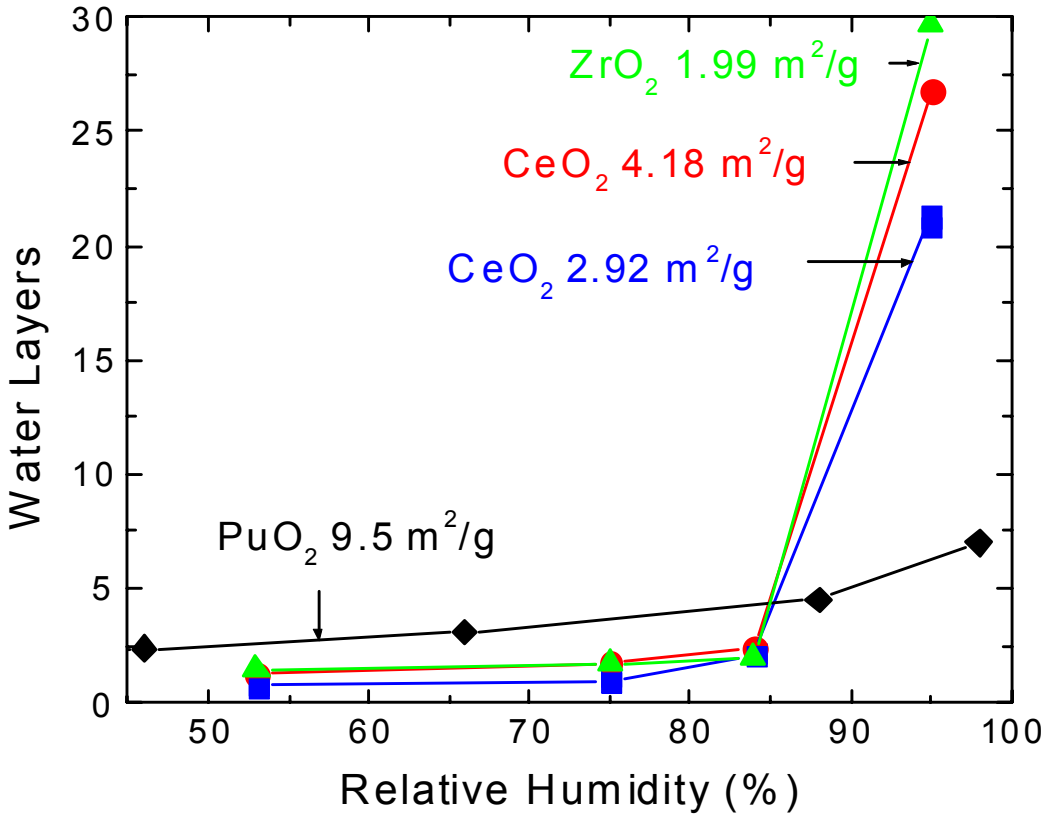
Adsorption / Desorption of Water

The oxide samples were completely dried by baking 24 hours at 500 ºC. Each oxide was previously characterized for its surface area using BET techniques (other work). Following baking, the samples were placed in constant humidity chambers and allowed to equilibrate. The amount of water adsorbed was determined by the weight change.

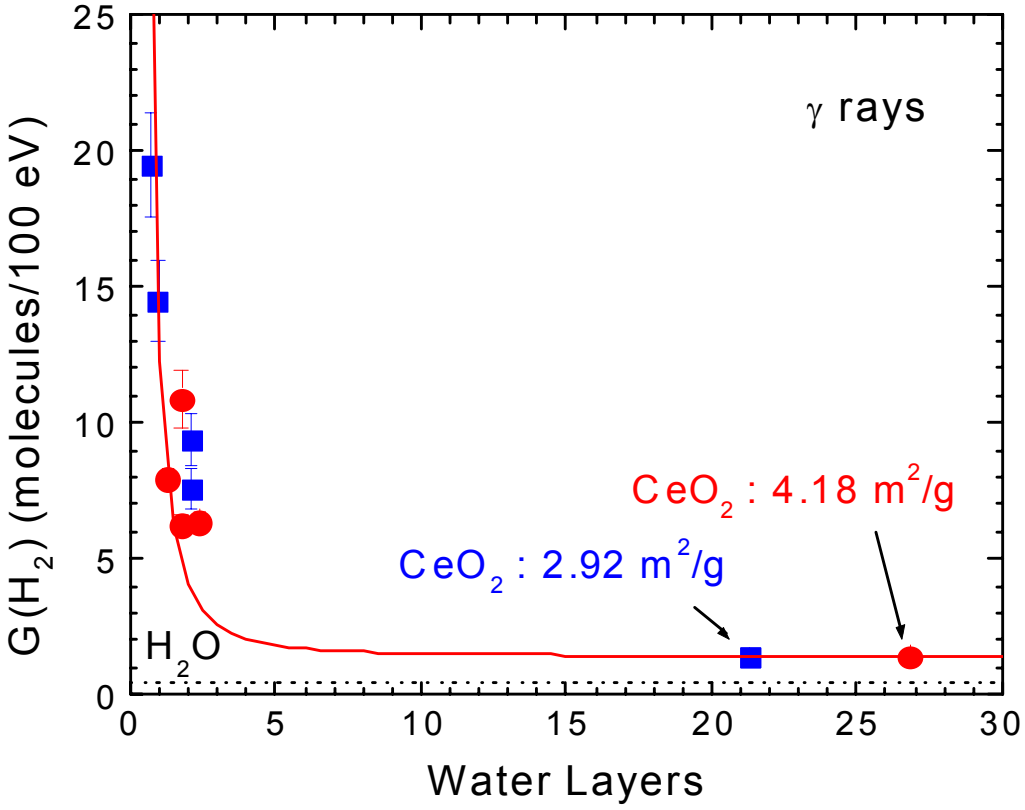
Several days were required for final equilibrium to be established in the adsorption of water. Desorption of water only took a few hours. Both adsorption and desorption were sufficiently slow that the sample could be manipulated for irradiation. The number of water layers is nearly independent of the surface area. Only 1-3 water layers exist up to a relative humidity of 80%. Multiple water layers occur at only the highest humidity.

Water Layer Dependence on Relative Humidity

PuO_2: A. Benhamou and J. P. Beraud *Analusis*, **8**, 376-380 (1980).
Assume 0.22 mg H_2O/m^2.



γ-Radiolysis of Water on CeO_2

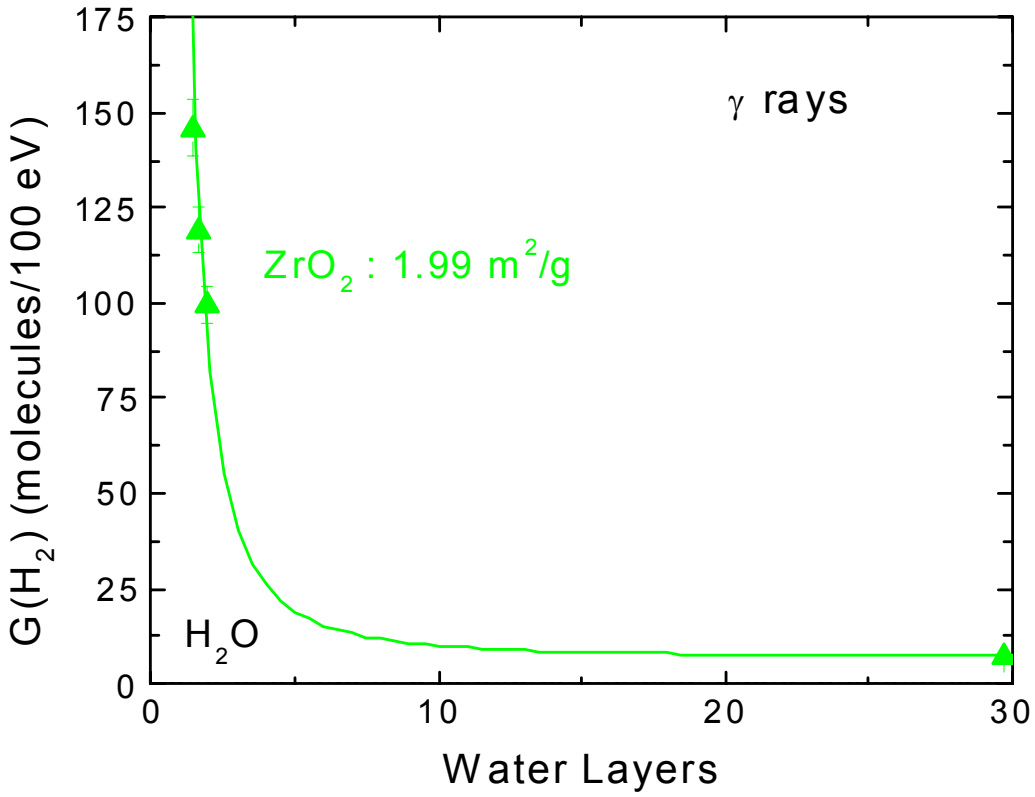


H_2 Yields with Respect to the Dose in Water

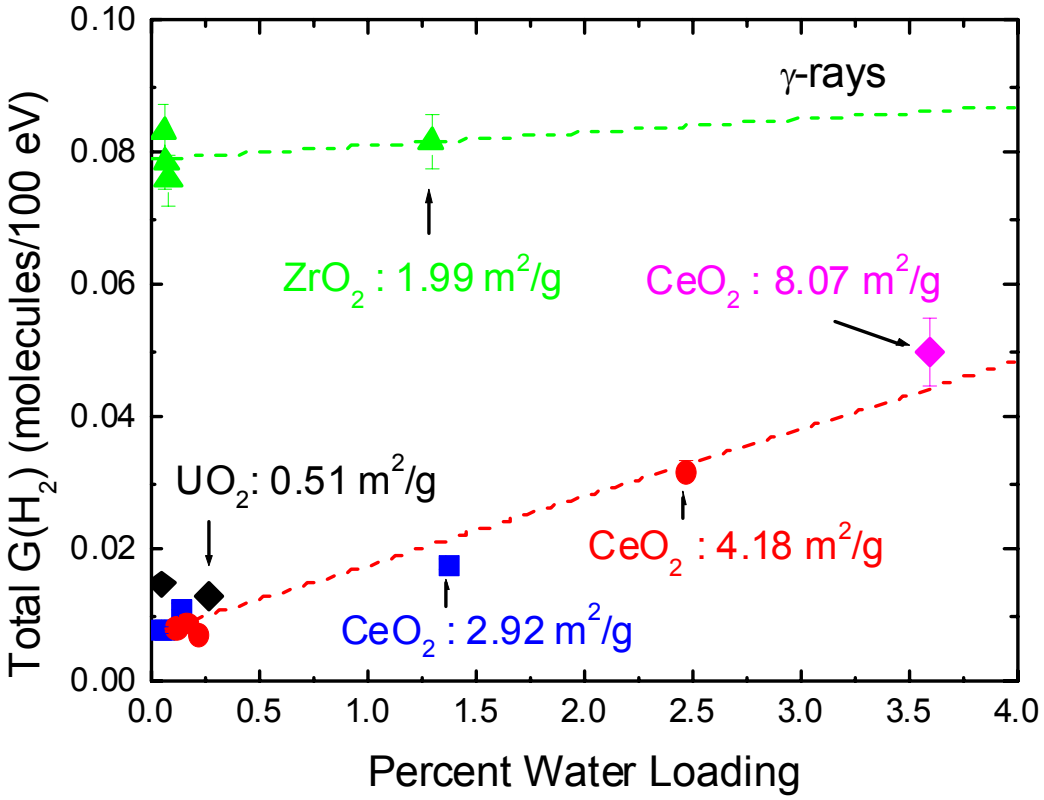
The γ-ray yields of H_2 with the maximum adsorbed water are 8.0 and 1.4 molecules/100 eV for ZrO_2 and CeO_2, respectively. This increase can be compared to the value of 0.45 molecule/100 eV for bulk water. **NOTE**: these G-values are determined relative to the energy deposited directly in the adsorbed water by the γ-rays. A difference in G-values from that of bulk water suggests modification of the chemistry or the escape of energy from the surface.

The yield of H_2 seems to be very dependent on the number of water layers and not the surface area. Low coverage of 1-2 water layers leads to an increase in G-values by over an order of magnitude from that of bulk water.

γ-Radiolysis of Water on ZrO_2



Total G-values for H_2 Production in γ-Radiolysis

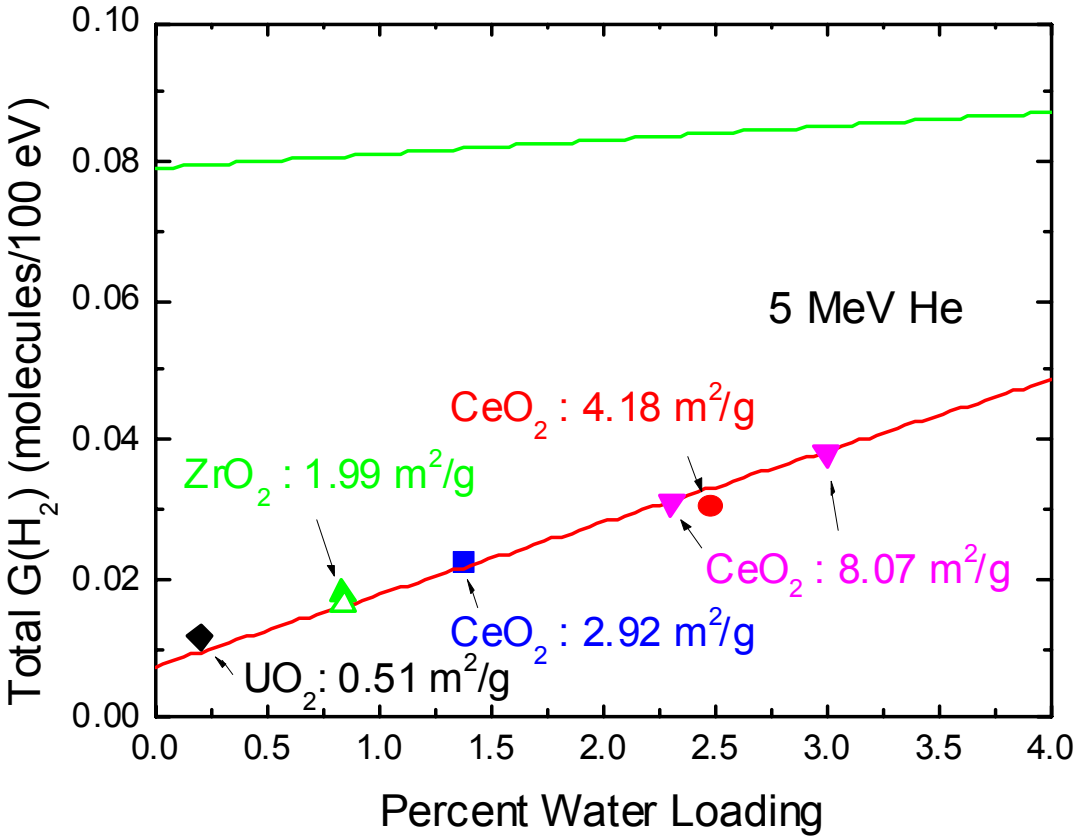


Total G-values for H_2 Production

The decrease in H_2 yields with increasing water loading may be due to a simple dilution effect. Calculation of the H_2 yields with respect to the total weight of the sample (H_2O and oxide) gives results that appear to be linearly dependent on water loading. There seems to be no effect due to the surface area, but ZrO_2 gives yields greater than the other oxides. **NOTE**: these G-values are determined relative to the total weight of the sample.

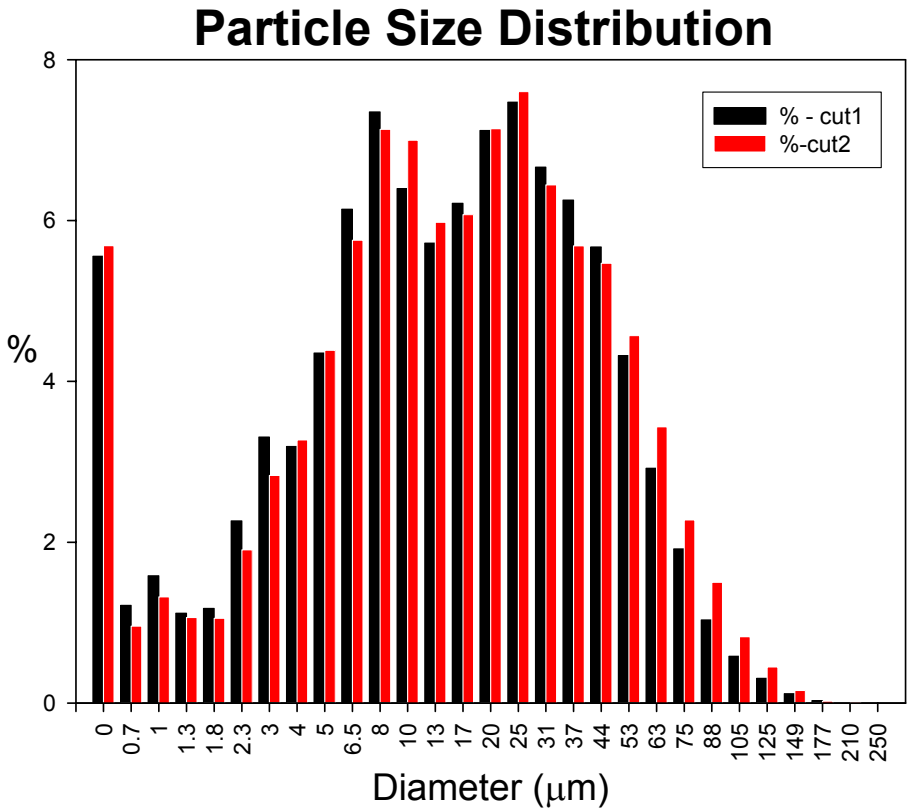
The results suggest an irreversible loss of energy from the oxide to the water. Energy loss in the bulk oxide creates electron/holes or excitons that migrate to the surface and react with the water. The less water to absorb this energy leads to an increase in the yield of H_2. This explanation assumes that the chemistry of the adsorbed water is nearly the same as in the bulk.

Total G-values for H_2 Production in α-Radiolysis



Estimation of Energy Escape from PuO_2

Measured particle size distribution is combined with range codes to estimate energy escaping through particle surface. At least 22% of the α particle energy is available at the surface in cut 1, more energy may be available if diffusion of active species is included.



Particle Size Range (μm)	Fraction of Energy Escaping from Particle	Mass Fraction in Size Range	Fraction of Energy Escaping from Particles of Origin
0 - 4	1.00	5.50563E-05	5.50563E-05
5 - 9	0.90	0.002053251	0.001847926
10 - 19	0.58	0.016578098	0.009615297
20 - 29	0.38	0.052240635	0.019851441
30 - 39	0.28	0.052483962	0.014695509
40 - 49	0.22	0.18663856	0.041060483
50 - 59	0.18	0.121014281	0.021782571
60 - 69	0.15	0.134055734	0.02010836
70 - 79	0.12		
80 - 89	0.11	0.681714175	0.074988559
90 - 149	0.08	0.274854718	0.021988377
≥150	0.06	0.043431106	0.002605866
			0.225993581

Measurement of Energy Escape from PuO_2

A microdosimetry laboratory is being set up at LANL to measure the energy escaping PuO_2 particles. Calibration and testing studies are currently underway.

Three devices are being used in these measurements:

Surface barrier detector – distribution of α-particle energies and fluence rate in air.

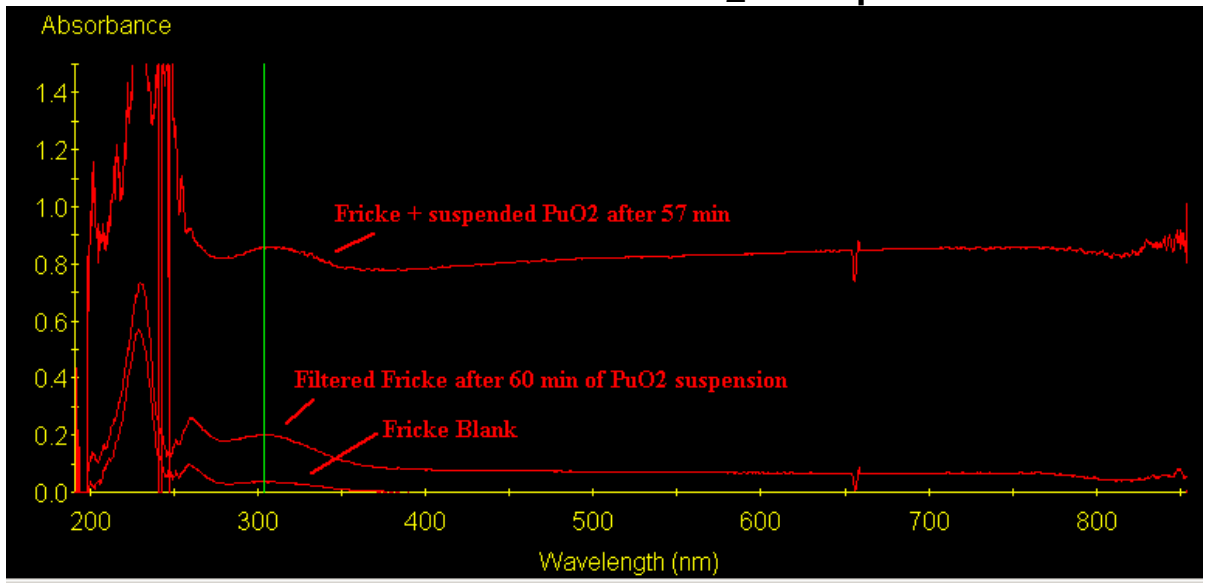
NaI & CdTe detector – estimate of γ dose rate (and total dose rate irrespective of particle size), Pu isotopics and total Pu content.

Ionization chamber – average α/β dose rate.

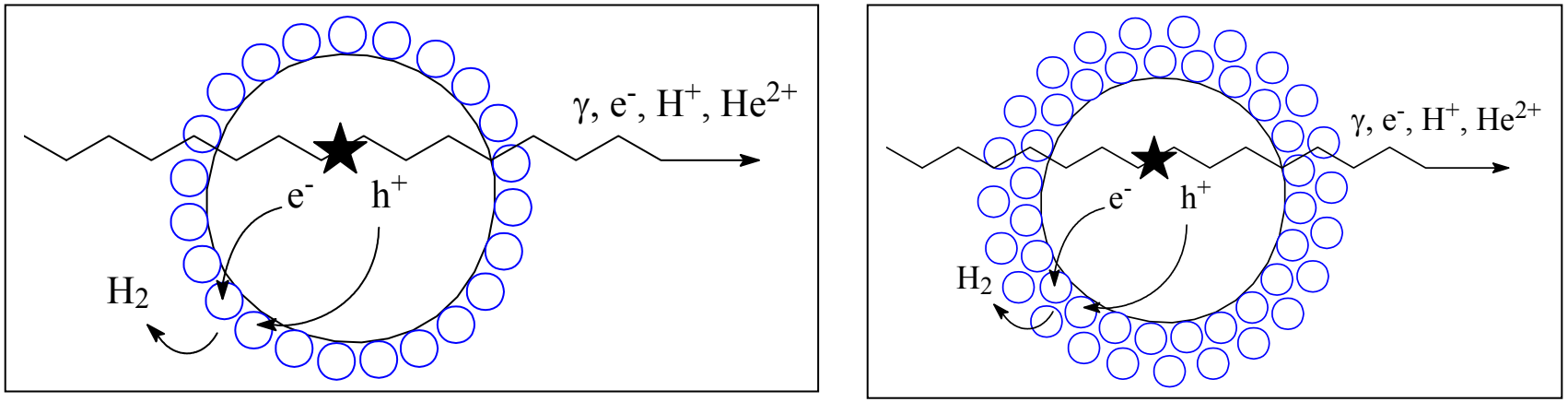
Measurement of Energy Escape from PuO_2

Chemical dosimeters are being developed to measure the total energy deposited in an aqueous solution by the PuO_2 particles. Appropriate systems are calibrated at Notre Dame and used at LANL. These experiments may eventually measure specific reactive species, i.e. e^- or OH radicals.

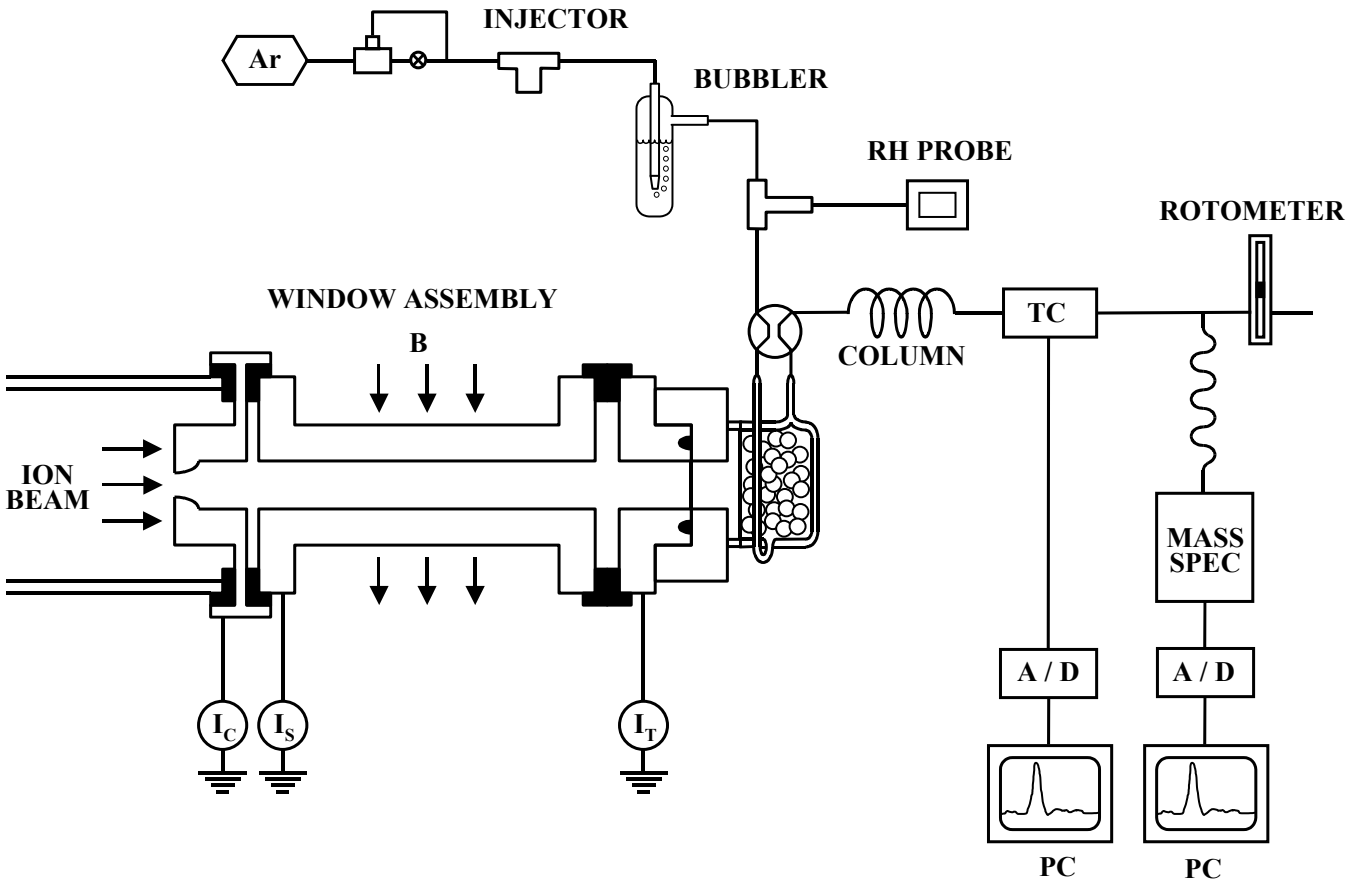
Response of Fricke Dosimeter in PuO_2 suspension.



H_2 Dependence on Water Loading



Heavy Ion Radiolysis Assembly



Acknowledgments

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